Supporting Information

One-Pot Synthesis of Polyvinylalcohol (PVA) Copolymers via Ruthenium Catalyzed Equilibrium Ring-Opening Metathesis Polymerization of Hydroxyl Functionalized Cyclopentene

Robert Tuba,[1] Mohammed Al-Hashimi,[1] Hassan S. Bazzi,[1] Robert H. Grubbs[1,2]**

[1]Department of Chemistry, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar. [2]The Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States.

*Email: rhg@caltech.edu; robert.tuba@tamu.edu.

Contents

1. General information

All reactions were conducted under argon atmosphere in a glovebox. Ruthenium catalysts **6** and **7** (Materia), cyclopentene (Aldrich), ethyl vinyl ether (Aldrich), cyclopentene, 1-hydroxy-3-cyclopentene, 1,6-heptadiene-4-ol (Aldrich), palladium on carbon (Aldrich), THF-d_8, toluene-d_8 (Cambridge Isotope or Aldrich) and other solvents, were used as received.

NMR experiments were performed at 10 - 40 ^{o}C. All NMR samples were stabilized at the given temperature for 10 min before data collection. All the NMR tubes were flame dried and evacuated *in vacuo* in advance. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 and Bruker Avance II 600 spectrometer in THF-d_8 and Toluene-d_8 and referenced to residual internal THF (δ = 1.73 ppm ^{1}H and 25.4 ppm ^{13}C) and toluene (δ = 2.09 ppm ^{1}H and 20.4 ppm ^{13}C). The quantitative ^{13}C NMR spectra for *cis*/*trans* bond ratio determination were recorded with inverse gated decoupling at 10 s relaxation delay.

GPC analyses were carried out using a Viscotek GPC Max VE 2001 instrument with a Viscotek TDA 302 triple array detector and Viscotek Org Guard column with three (in series) Mixed Medium columns (LT5000L) at 35 °C and a flow rate of 1.0 mL/min. A 12-point Universal Calibration Standard calibration curve was recorded.

2. Theoretical calculations

The ring strain energy of a series of substituted cyclopenetene have been calculated with density functional theory studies performed with RB3LYP method at 6-31G (D) basis set using SPARTAN '10 MECHANICS PROGRAM: PC/x86 1.1.0.software.

Example for cyclopentene ΔE (kcal/mol) calculation:

Energy (Hartree):

A: -195.333677; B: -78.588104; C: -273.930443

$\Delta E = E_c-(E_a+E_b)$

ΔE (Hartree) = -273.930443 - (-195.333677-78.588104) = - 0.008662 Hartree

1 Hartree = 627.5 kcal/mol

ΔE (kcal/mol) = - 0.008662 * 627.5 = **-5.44 kcal/mol**

Table S1. Calculated ring strain energy, atomic charge values on C0 and C4 carbon atoms (Electrostatic, Mulliken and Natural) and double bond orders for different cyclopentene derivatives. Solvation: toluene [SM8].*

cyclopentene derivatives	Atomic charges (C0)			Atomic charges (C4)			Atomic charges (average)			Bond order	Energy (Hartree)			ΔH (kcal/mol)
	Electrostatic	Mulliken	Natural	Electrostatic	Mulliken	Natural	Electrostatic	Mulliken	Natural		Cyclopentene derivative	Ethylene	1,6-heptadiene derivative	
2-OH	-0.172	-0.118	-0.229	-0.160	-0.116	-0.224	-0.166	-0.117	-0.227	1.958	-270.54342	-78.588104	-349.142307	-6.77
3-OH	-0.094	-0.112	-0.199	-0.258	-0.110	-0.250	-0.176	-0.111	-0.225	1.937	-270.542879	-78.588104	-349.141346	-6.50
2-ethyleneketal	-0.215	-0.123	-0.226	-0.217	-0.122	-0.225	-0.216	-0.123	-0.226	1.947	-423.179218	-78.588104	-501.777224	-6.21
CP	-0.192	-0.121	-0.229	-0.192	-0.121	-0.229	-0.192	-0.121	-0.229	1.959	-195.333677	-78.588104	-273.930443	-5.44
3-NH_2	-0.141	-0.124	-0.216	-0.306	-0.106	-0.234	-0.224	-0.115	-0.225	1.959	-250.675658	-78.588104	-329.272346	-5.39
2-NH_2	-0.289	-0.120	-0.225	-0.120	-0.124	-0.228	-0.205	-0.122	-0.227	1.947	-250.676942	-78.588104	-329.273352	-5.21
2-CH_2OH	-0.077	-0.121	-0.227	-0.338	-0.126	-0.224	-0.208	-0.124	-0.226	1.954	-309.855058	-78.588104	-388.450968	-4.90
3-Cl	-0.142	-0.105	-0.187	-0.210	-0.088	-0.253	-0.176	-0.097	-0.220	1.918	-654.934246	-78.588104	-733.529339	-4.39
3-ethyleneketal	-0.069	-0.126	-0.191	-0.465	-0.112	-0.268	-0.267	-0.119	-0.230	1.904	-423.180589	-78.588104	-501.774674	-3.75
2-Cl	-0.181	-0.119	-0.222	-0.181	-0.119	-0.222	-0.181	-0.119	-0.222	1.945	-654.93254	-78.588104	-733.526580	-3.72
3-CH_2OH	-0.054	-0.129	-0.217	-0.388	-0.119	-0.232	-0.221	-0.124	-0.225	1.938	-309.855564	-78.588104	-388.448664	-3.13
3-TMS	-0.187	-0.133	-0.240	-0.254	-0.131	-0.226	-0.221	-0.132	-0.233	1.926	-604.005309	-78.588104	-682.597818	-2.76
2-on	-0.201	-0.118	-0.225	-0.201	-0.118	-0.225	-0.201	-0.118	-0.225	1.942	-269.350053	-78.588104	-347.940244	-1.31
2-TMS	-0.209	-0.127	-0.227	-0.209	-0.126	-0.227	-0.209	-0.126	-0.227	1.957	-604.004267	-78.588104	-682.592563	-0.12
3-on	-0.046	-0.094	-0.124	-0.362	-0.151	-0.338	-0.204	-0.123	-0.231	1.796	-269.359531	-78.588104	-347.947446	0.12
3-tBu	-0.116	-0.133	-0.217	-0.406	-0.117	-0.230	-0.261	-0.125	-0.224	1.934	-352.587818	-78.588104	-431.174221	1.07
2-tBu	-0.228	-0.124	-0.223	-0.228	-0.124	-0.223	-0.228	-0.124	-0.223	1.953	-352.586957	-78.588104	-431.170272	3.01

*Based on the software report the cyclopentene species are named according to the following structure:

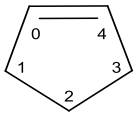

Table S2. Calculation report example for cyclopentene (**1**).

SPARTAN '10 MECHANICS PROGRAM: PC/x86 1.1.0
Frequency Calculation
Reason for exit: Successful completion
Mechanics CPU Time : .02
Mechanics Wall Time: .05
SPARTAN '10 Quantum Mechanics Program: (PC/x86) Release 1.1.0v4
Job type: Geometry optimization.
Method: RB3LYP
Basis set: 6-31G(D)
Number of shells: 36
Number of basis functions: 91
Multiplicity: 1
SCF model:
A restricted hybrid HF-DFT SCF calculation will be
performed using Pulay DIIS + Geometric Direct Minimization
Solvation: toluene [SM8]
Optimization:
Step Energy Max Grad. Max Dist.
1 -195.331799 0.021925 0.086707
2 -195.333632 0.004196 0.035797
3 -195.333677 0.000269 0.000540
Reason for exit: Successful completion
Quantum Calculation CPU Time : 38.00
Quantum Calculation Wall Time: 38.48
SPARTAN '10 Properties Program: (PC/x86) Release 1.1.0
Atomic Charges:
Electrostatic Mulliken Natural
1 C0 : -0.192 -0.121 -0.229
2 C1 : -0.017 -0.307 -0.488
3 C2 : -0.210 -0.286 -0.459
4 C3 : -0.017 -0.307 -0.488
5 C4 : -0.192 -0.121 -0.229
6 H1 : +0.124 +0.131 +0.232
7 H2 : +0.060 +0.147 +0.237
8 H3 : +0.050 +0.147 +0.241
9 H4 : +0.069 +0.144 +0.240
10 H5 : +0.093 +0.147 +0.235
11 H6 : +0.060 +0.147 +0.237
12 H7 : +0.050 +0.147 +0.241
13 H8 : +0.124 +0.131 +0.232
Bond Orders Mulliken
1 C0 C1 : 1.011
2 C0 C4 : 1.959

3 C0 H1 : 0.929
4 C1 C2 : 1.000
5 C1 H2 : 0.930
6 C1 H3 : 0.936
7 C2 C3 : 1.000
8 C2 H4 : 0.944
9 C2 H5 : 0.948
10 C3 C4 : 1.011
11 C3 H6 : 0.930
12 C3 H7 : 0.936
13 C4 H8 : 0.929
Reason for exit: Successful completion
Properties CPU Time : .22
Properties Wall Time: .22

3. Thermodynamic investigation of equilibrium ring opening metathesis polymerization of 2

An NMR tube was charged with catalyst **6** (4.5 mg; 0.00530 mmol) or **7** (3.3 mg; 0.00564 mmol) and 3-cyclopentene-1-ol (**2**) in a 2.275 M THF-d_8 stock solution (1.0 mL solution; 2.275 mmol **2**). Then the NMR sample was inserted into the precooled (10 °C) NMR instrument. Following equilibration time (60 – 90 min) ^{1}H NMR was recorded. The temperature increased with 5 °C or 10 °C increments. The measurement was repeated up to 40 °C. ^{1}H NMR spectra were recorded for each reaction temperature (catalyst **7** Figure S1 – S5; catalyst **6** Figure S6 – S9) and the conversion was determined according to the ratio of the integrals of the peaks at 5.56 ppm (**2**, CH, s) and 5.46 ppm (**4**, CH, br, s).

Thermodynamic data calculation. (See also Table 1. and Figure 2.) According to the equilibrium polymerization theory, the thermodynamic data were calculated from the following relationships:

$$\boldsymbol{ln}[\boldsymbol{M}] = \frac{\Delta H}{R * T} - \frac{\Delta S}{R} \qquad (1)$$

where [M] is the monomer equilibrium concentration, ΔH is the activation enthalpy (kJ mol^{-1}) during the polymerization, R is the universal gas constant (8.3144 J·mol^{-1}·K^{-1}), T is the absolute temperature in degrees Kelvin (K) and ΔS is the activation entropy (J·mol^{-1}·K^{-1}). ΔH can be calculated from the slope of the line in Figure 1. (m = −3.12 · 10^3 K) according to the following equation (1 kcal = 4.184 kJ):

(2)

$$\Delta \boldsymbol{H} = m \cdot R$$

$$\Delta \boldsymbol{H} = -3.12 \cdot 10^3 K \cdot 8.31\, J \cdot mol^{-1} \cdot K^{-1} = \boldsymbol{-25.93\ kJ \cdot mol^{-1}}$$

$$\Delta \boldsymbol{H} = \boldsymbol{-6.2\ kcal \cdot mol^{-1}}$$

The standard entropy change can be calculated by the rearrangement of equation (1):

$$\Delta S = \frac{\Delta H}{T} - R \cdot \ln [M]$$

$$\Delta S = \frac{-25930\, J \cdot\ mol^{-1}}{293\ K} - 8.31 \cdot \ln[0.325] = \boldsymbol{-79.16\, J \cdot mol^{-1} \cdot K^{-1}} \quad (3)$$

$$\Delta \boldsymbol{S} = \boldsymbol{-18.9\ cal \cdot mol^{-1}\ \cdot K^{-1}}$$

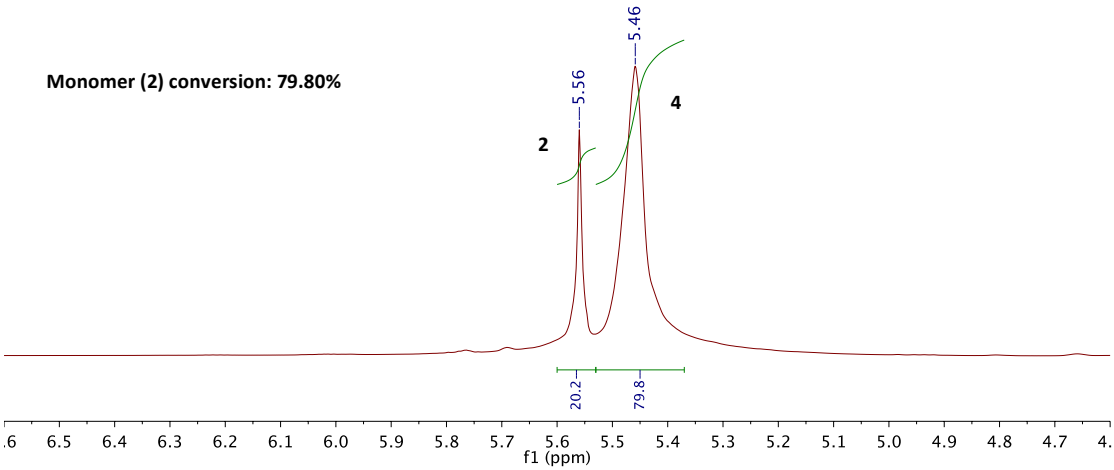

Figure S1. *In-Situ* ^{1}H NMR spectrum of the equilibrium reaction mixture of **2** and **4** in THF-d_8 at 30 °C. THF-d_8; [**2**] = 2.28 M; 0.23 mol% **7**. (VT-^{1}H NMR).

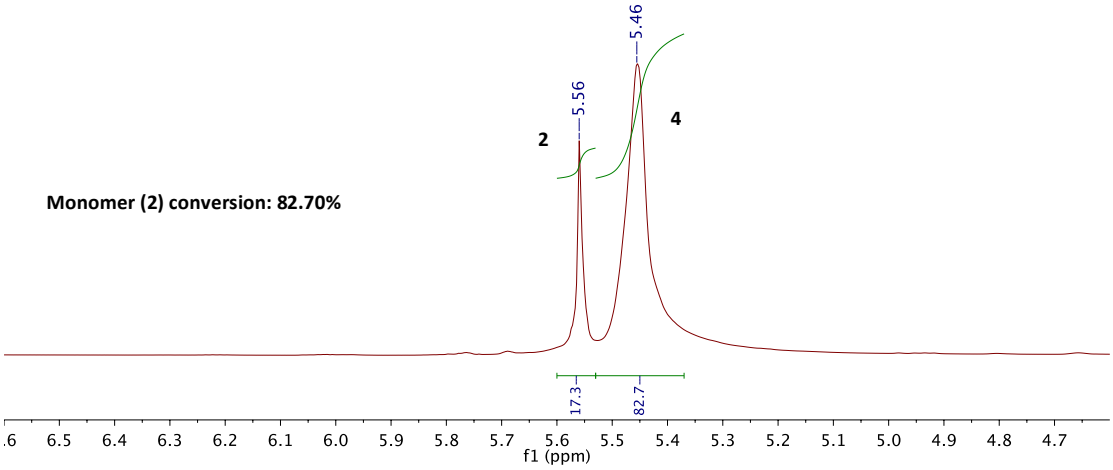

Figure S2. *In-Situ* ^{1}H NMR spectrum of the equilibrium reaction mixture of **2** and **4** in THF-d_8 at 25 °C. THF-d_8; [**2**] = 2.28 M; 0.23 mol% **7**. (VT-^{1}H NMR).

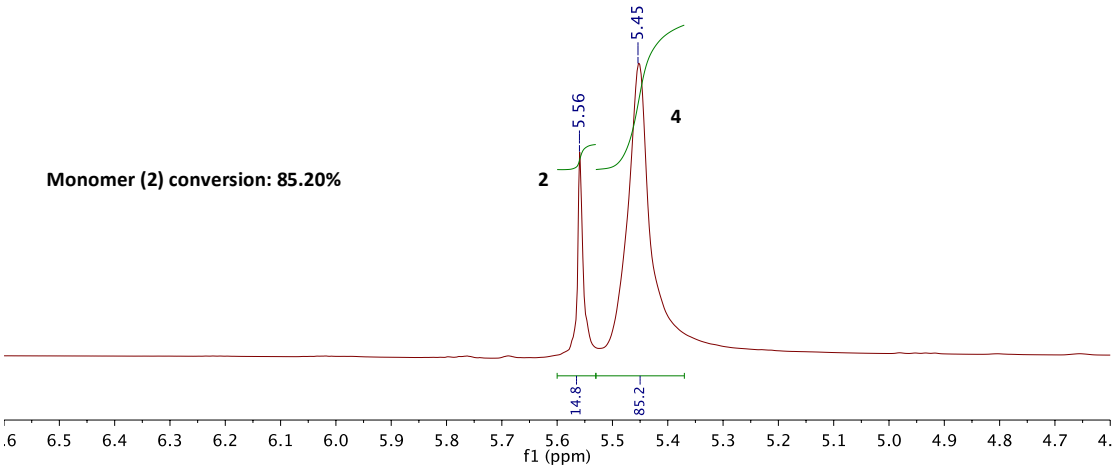

Figure S3. *In-Situ* ^{1}H NMR spectrum of the equilibrium reaction mixture of **2** and **4** in THF-d_8 at 20 °C. THF-d_8; [**2**] = 2.28 M; 0.23 mol% **7**. (VT-^{1}H NMR).

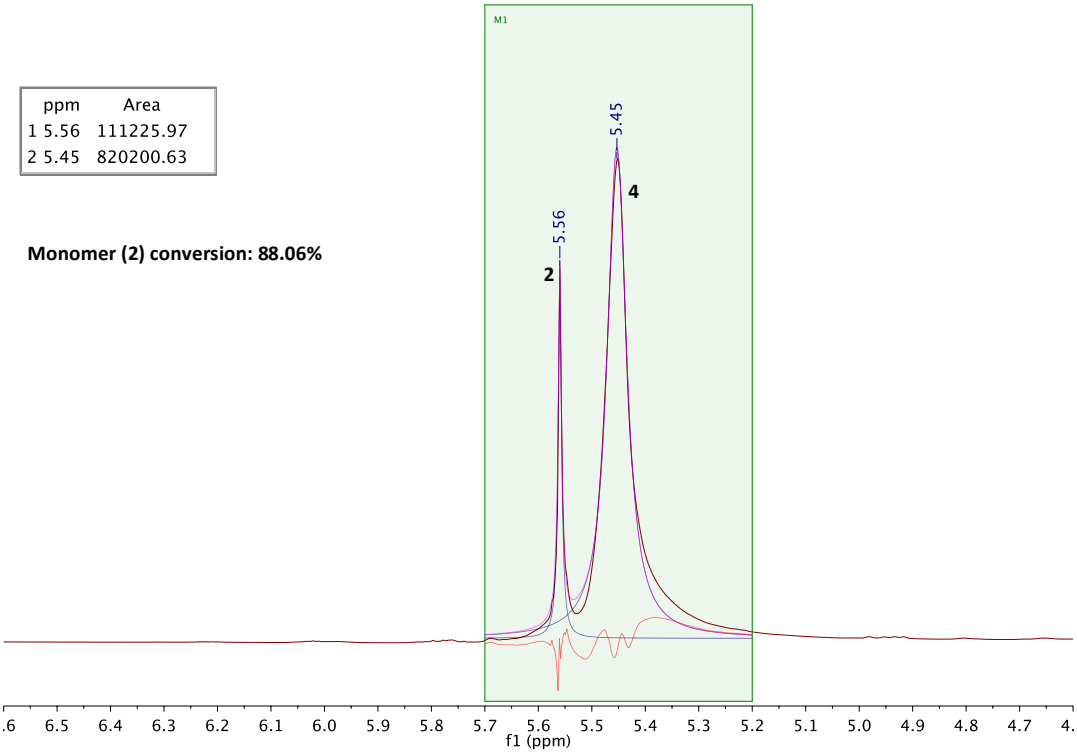

Figure S4. *In-Situ* ^{1}H NMR spectrum of the equilibrium reaction mixture of **2** and **4** in THF-d_8 at 15 °C. THF-d_8; [**2**] = 2.28 M; 0.23 mol% **7**. (VT-^{1}H NMR).

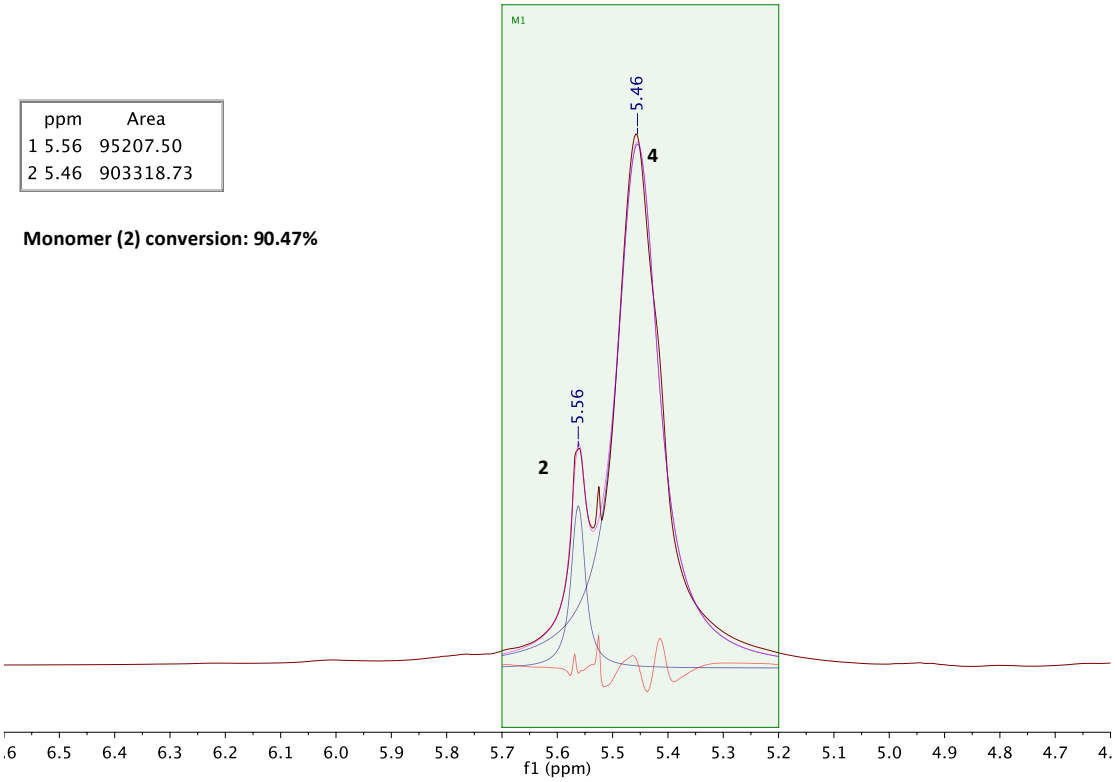

Figure S5. *In-Situ* ^{1}H NMR spectrum of the equilibrium reaction mixture of **2** and **4** in THF-d_8 at 10 °C. THF-d_8; [**2**] = 2.28 M; 0.23 mol% **7**. (VT-^{1}H NMR).

4. Synthesis of 4 by ROMP of 2

Following the thermodynamic investigation, the catalyst was allowed to decompose on standing. The decomposition mixture was suspended in MeOH (1.0 mL) and transferred into a vial (20 mL). The solvent was concentrated in *vacuo*, and the remaining waxy orange solid was dissolved in THF (1.5 mL). The THF solution was poured into *n*-hexane (5.0 mL), which precipitated the orange polymer. The supernatant was removed by a syringe and washed with additional hexane (2 x 2 mL). Then the polymer was concentrated in *vacuo* giving a waxy orange solid (119.4 mg; 63.2% - assuming the 17.4% monomer equilibrium concentration at 25 °C the isolated yield is 76.7%).

^{1}H NMR (THF-d_8): δ 5.52 (s, 2H, =C*H*-), 3.60 – 3.30 (br multiple peaks, 2H, C*H* and O*H*), 2.15 (br s, 4H, CH_2). ^{13}C{^{1}H} NMR (THF-d_8): δ 130.20 (*trans*, =*C*H-), 129.14 (*cis*, =*C*H-), 71.76 (*trans*, *C*H-OH), 71.13 (*cis*, *C*H-OH), 42.44 (*cis*, *C*H$_2$), 41.57 (*trans*, *C*H$_2$). M_n = 3.76 kDa, Đ = 1.57

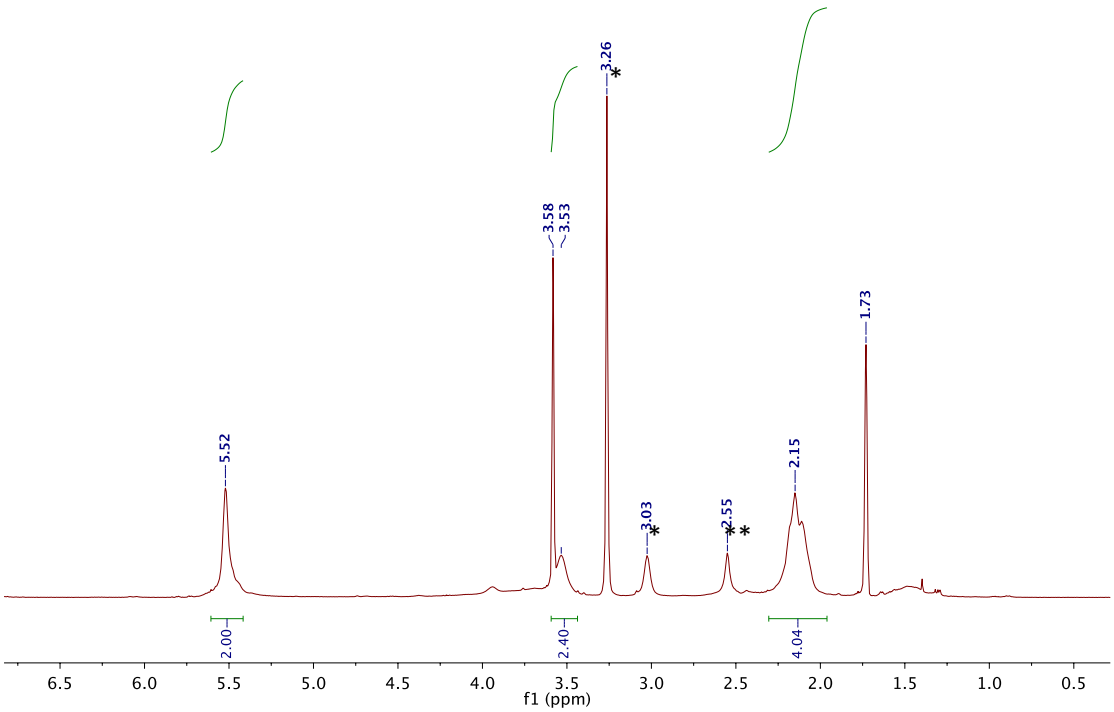

Figure S6. ^{1}H NMR spectra of **4** (THF-d_8). *MeOH solvent, **H_2O impurities. 1.73 and 3.58 ppm THF-d_8.

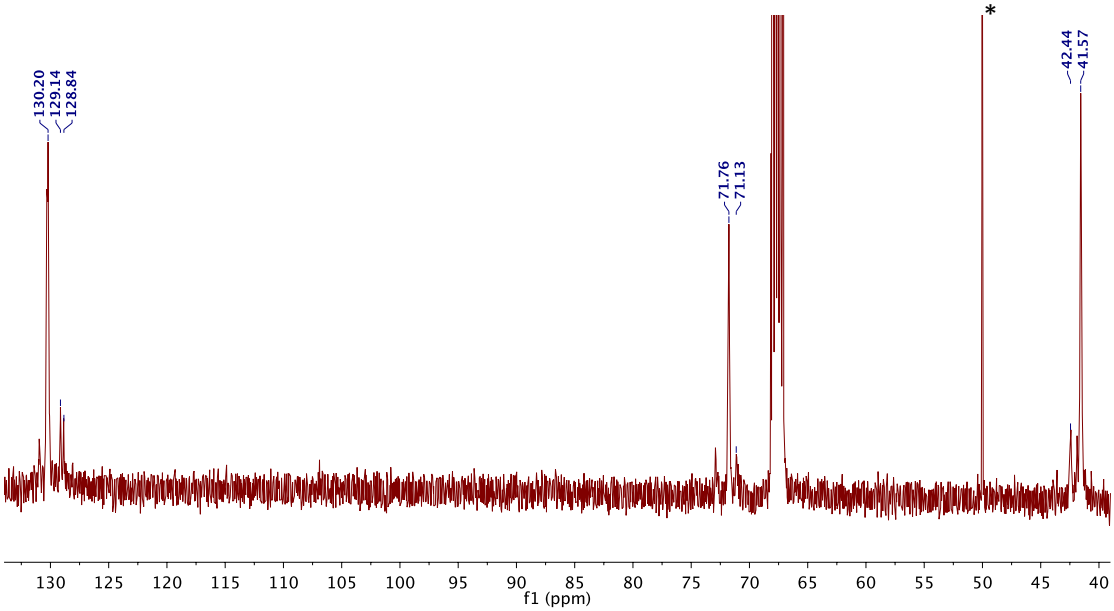

Figure S7. ^{13}C NMR spectra of **4** (THF-d_8). *MeOH solvent residue.

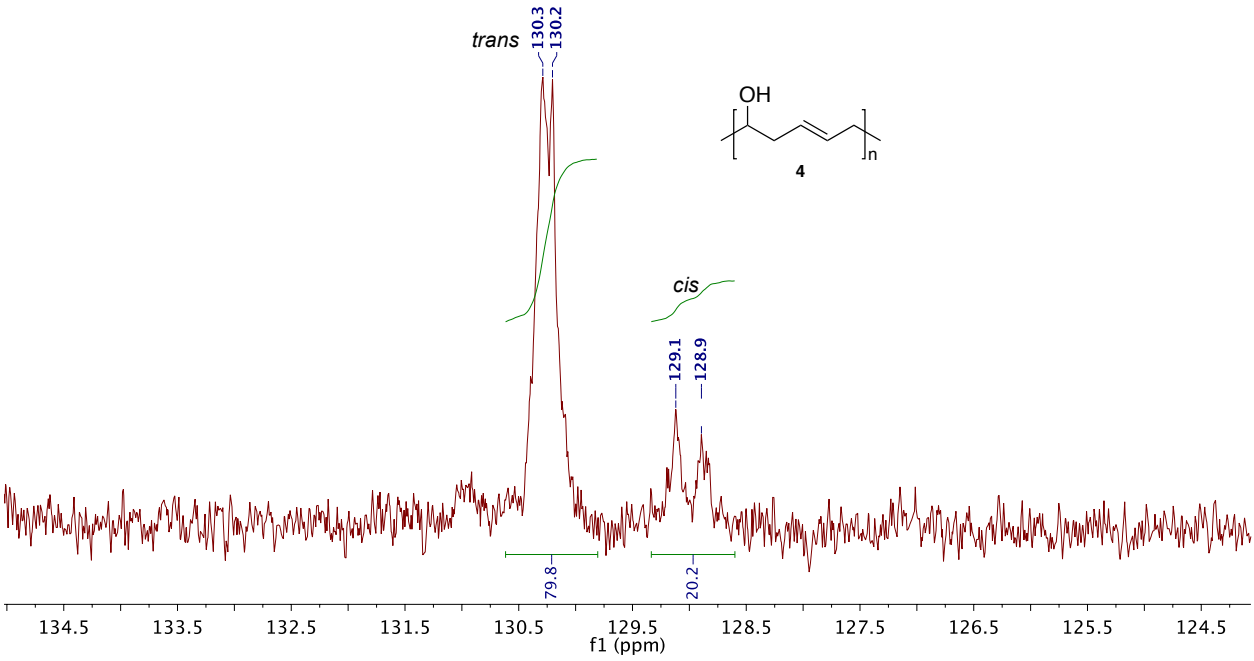

Figure S8. Quantitative ^{13}C NMR spectrum - illustrating *cis*/*trans* ratio of the isolated poly(vinylalcohol-*alt*-propenylene) (THF-d_8).

5. Synthesis of 4 by ADMET of 10

In a glove box a vial (7 mL) was charged with catalyst **7** (10.0 mg; 0.016 mmol) and THF (3.70 mL). Then **10** (1.6 mL; 12.27 mmol) was added by syringe. The reaction was carried out in an open vial. Following the addition of **10**, immediate ethylene evolution was observed. The solution was transparent and had an intense orange color. After two hours reaction time, 0.3 mL ethyl vinyl ether was added. The mixture was stirred for additional 10 minutes and transferred to a vessel charged with n-hexane (5 mL), which precipitated the orange polymer. The supernatant was removed by syringe. The remaining waxy solid was washed with *n*-hexane (2 x 2 mL) and concentrated in *vacuo* giving a waxy orange solid. This solid was dissolved in THF with gentle heating and poured into *n*-hexane (5.0 mL). This precipitation procedure was repeated four times. The remaining precipitate was then concentrated in *vacuo*, giving an orange solid (714.9 mg; 68.0% - assuming the 17.4% monomer equilibrium concentration at 25 ^{o}C, the isolated yield is 82.4%). M_n = 2.78 kDa, Đ = 1.38.

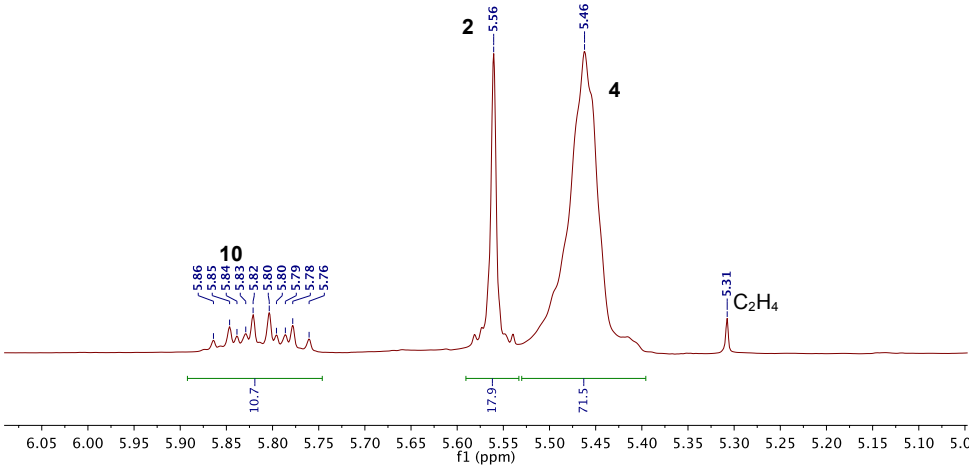

Figure S9. [1]H NMR spectra of the reaction mixture [**10**] = 2.30 M, 27 ºC, **6** = 0.22 mol%, THF-d_8, t_r = 1h.

6. Hydrogenation of poly(vinylalcohol-*alt*-propenylene)

A Schlenk vessel (50 mL) was charged with **4** (124.37 mg) and methanol (5 mL). Once the polymer was solubilized, Pd/C (85.2 mg) was added (5% palladium per double bond). The black suspension-containing vessel was flushed with Ar three times and then placed under vacuum. Then a balloon filled with hydrogen was connected to the vessel. After 2 hours reaction time the orange supernatant became colorless. The mixture was stirred for an additional 22 h at room temperature. Then the black suspension was filtered through a double filter paper. The vessel and filter paper were washed with hot methanol (250 mL). The collected filtrate was concentrated in *vacuo*, giving **11**[1]as a white powder (90.3 mg, 73%).

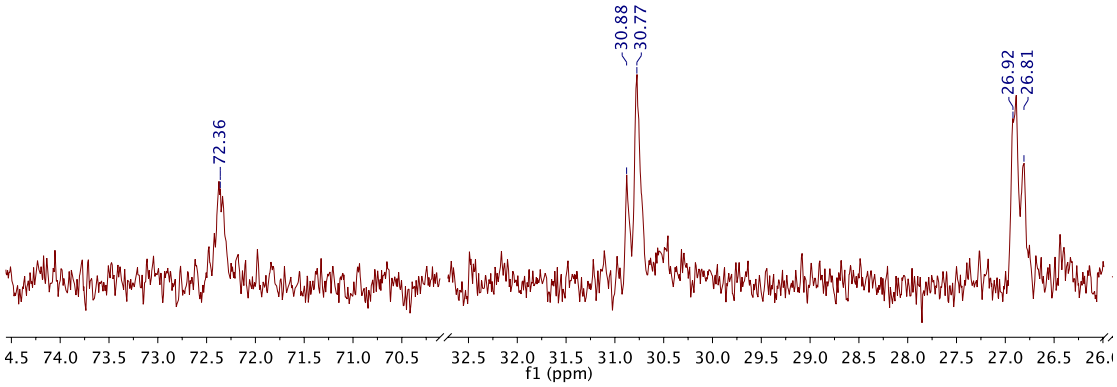

Figure S10. [13]C NMR spectra of the isolated **11**.

[1] Li, Z.-L.; Lv, A.; Li, L.; Deng, X.-X.; Zhang, L.-J.; Du, F.-S.; Li, Z.-C. *Polymer*, **2013**, *54*, 3841.

7. Copolymerization of 1 with 2

A screw-capped NMR tube was charged with THF-d_8 (0.4 mL), **1** (0.1 mL; 1.085 mmol) and **2** (0.09 mL; 1.139 mmol). Then THF-d_8 solution (0.4 mL) of **7** (3.3 mg; 0.00527 mmol) was added. The green catalyst solution gradually turned orange and became more viscous. ^{1}H NMR spectra were recorded at 0.5, 1 and 3h reaction times. Then 0.1 mL ethyl vinyl ether was added. The contents of the NMR tube were poured into a vial (15 mL) and precipitated with *n*-hexane (4 mL) with immediate polymer precipitation observable. The supernatant was removed by syringe and the remaining precipitate was dried in *vacuo* giving a yellow solid (111.23 mg; 64.0% - assuming a 27.6% monomer equilibrium concentration at 25 ^{o}C, the isolated yield is 88.3%). M_n = 11.1 kDa, Đ = 1.71.

^{1}H NMR (THF-d_8): δ 5.7 – 5.2 (br multiple peaks, 2H, =C*H*-), 3.60 – 3.30 (br multiple peaks, 2H, C*H* and O*H*), 1.80 – 2.30 (br multiple peaks, 4H, CH_2), 1.20 – 1.50 (br multiple peaks, 0.5 H, CH_2). ^{13}C{^{1}H} NMR (THF-d_8): δ 133.02 (C5), 131.33 (C8), 130.33 (C3), 128.47 (C4), 71.86 (br, C1 and C1*), 41.51 (br, C2 and C2*), 33.26 (C7*), 33.15 (C7), 30.69 (br, C6 and C6*).

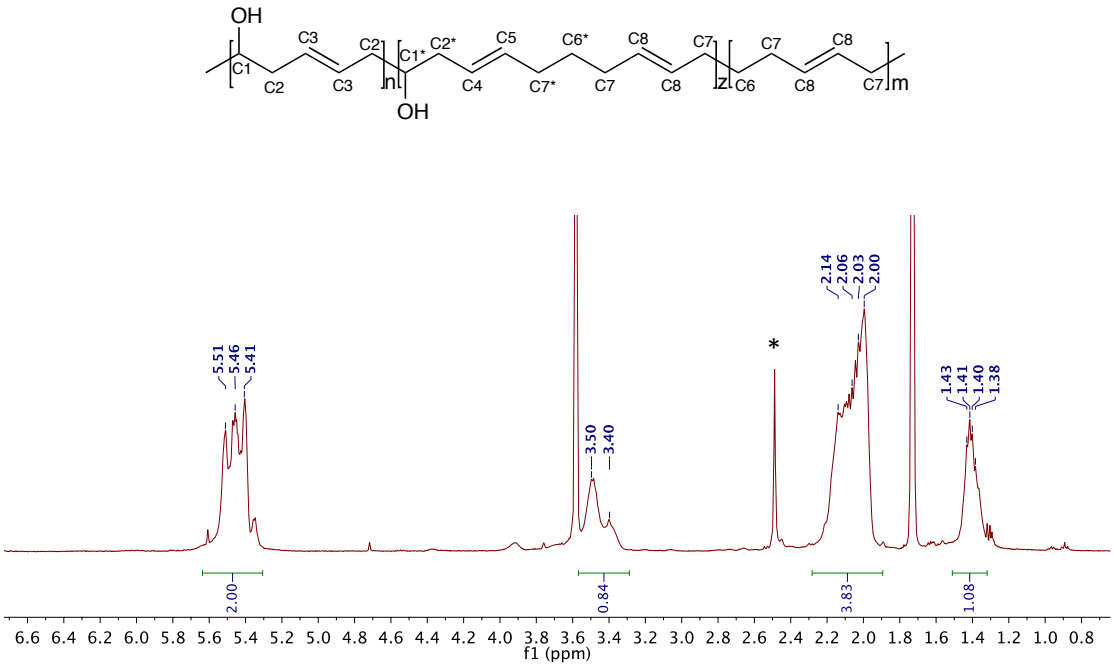

Figure S11. ^{1}H NMR spectra of the polymer synthesized by the copolymerization of **1** and **2** (THF-d_8). *H_2O traces.

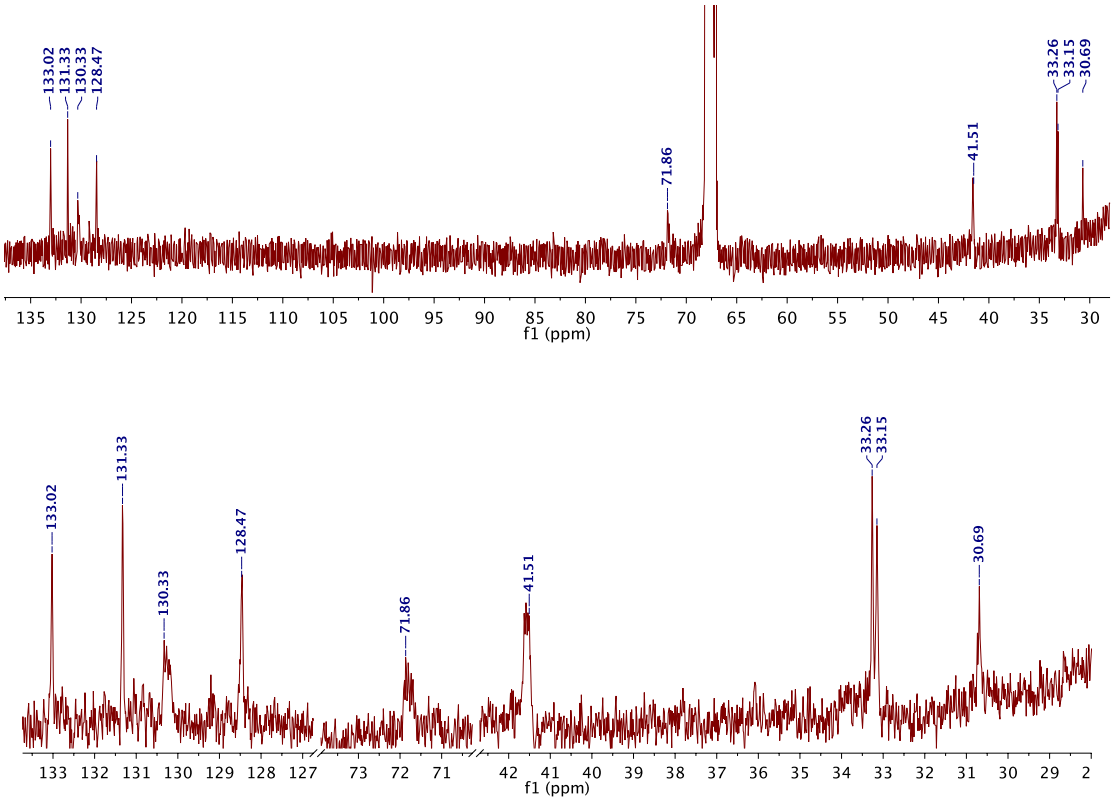

Figure S12. ^{13}C NMR spectra of the polymer synthesized by the copolymerization of **1** and **2** (THF-d_8).

Table S3. Conversion, M_n and molecular mass distributions (Đ) data for the homopolymers and copolymers. [**M**] = 2.17 M; 0.23 mol% catalyst; t_r = 1h, 27 – 30 ºC, THF or toluene.

Polymer	Catalyst	Monomer	Conversion [**1**] (%)	M_n (kDa)	M_n (kDa) Theorethically calculated	Đ
3[2]	**6**	**1**	50.0	15.4	14.8	2.07
3+4	**7**	**1 + 2**[a]	64.9	11.1	21.5	1.71
4	**7**	**2**	79.8	3.76	29.2	1.57

[a]The **1:2** monomer ratio was 50:50, the overall concentration was 2.17 M

[2] Tuba, R.; Grubbs, R. *Polymer Chemistry* **2013**, *4*, 3959.

8. *In-situ* ^{1}H NMR investigation of copolymerization of 1,6-heptadiene-4-ol 10 with cyclopentene

In a glovebox, a vial was charged with THF-d_8 (0.4 mL), **1** (0.1 mL; 1.130 mmol) and **10** (0.15 mL; 1.150 mmol). Then THF-d_8 solution (0.4 mL) of **6** (4.5 mg; 0.00530 mmol) was added. The mixture was stirred for one hour in an open vial. Rapid formation of ethylene gas was observed as the purple catalyst solution gradually turned to orange and became more viscous. Then the mixture was transferred into a screw-capped NMR tube and ^{1}H NMR spectra were recorded.

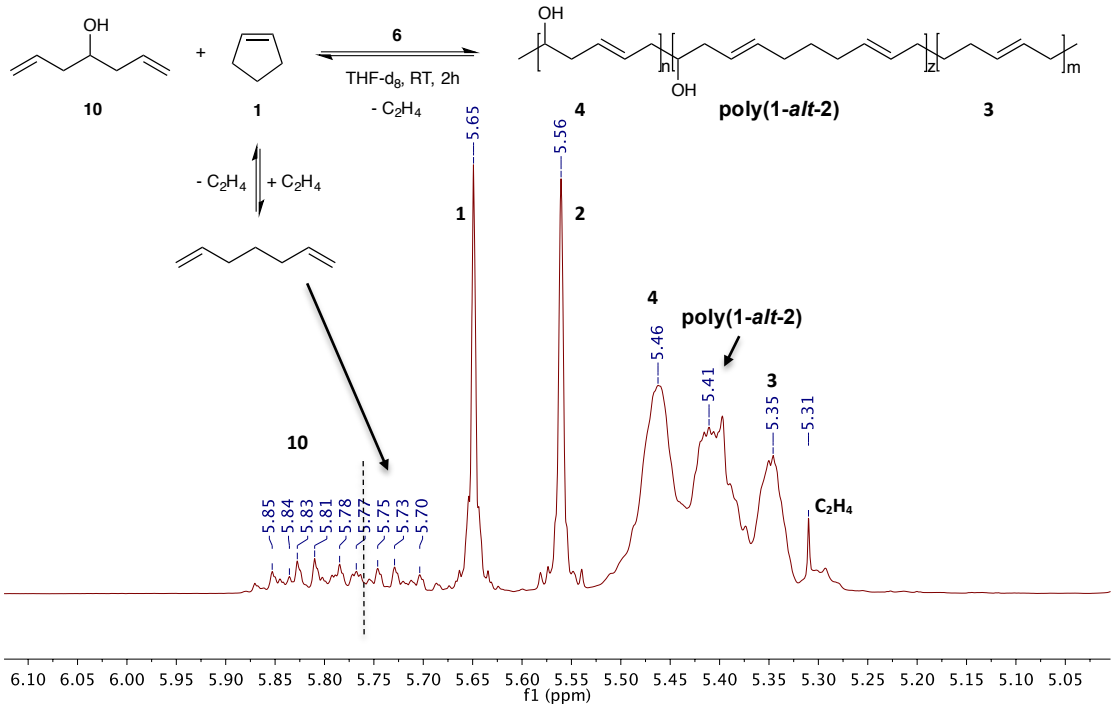

Figure S13. ^{1}H NMR spectrum of the reaction mixture (–CH= region) obtained by the copolymerization of **1** and **10** at RT. THF-d_8; [**1**] = 1.13 M; [**10**] = 1.15 M; 0.23 mol% **6**.

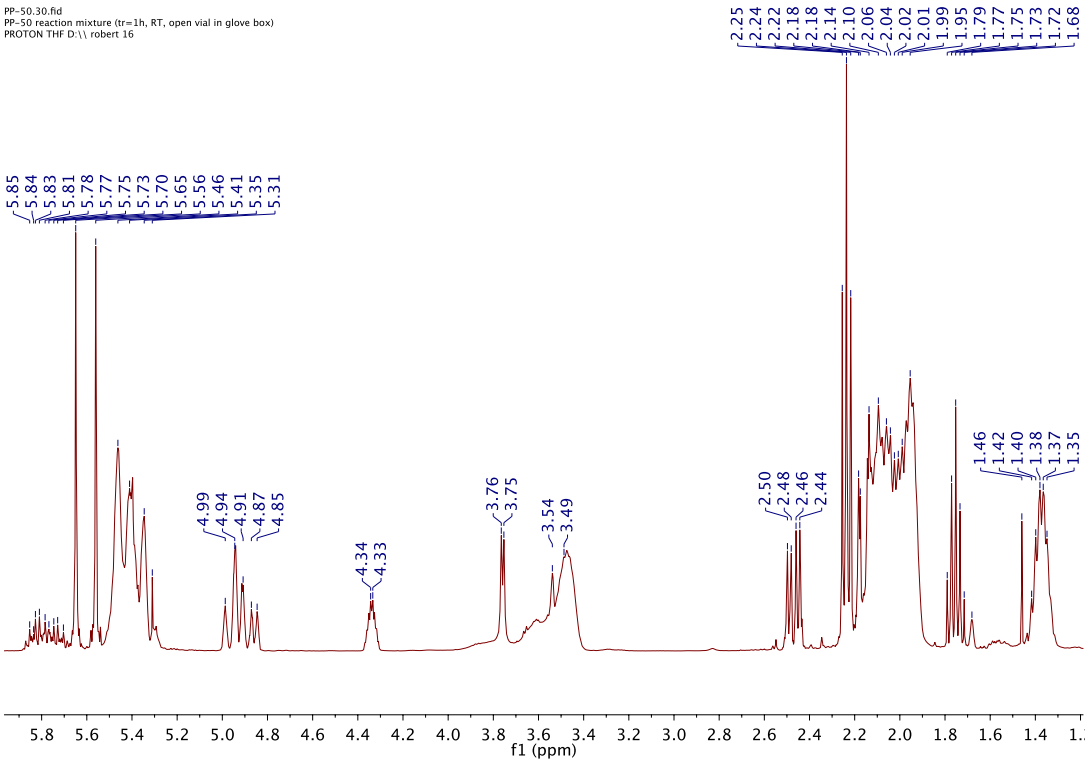

Figure S14. ^{1}H NMR spectrum of the reaction mixture obtained by the copolymerization of **1** and **10** at RT. THF-d_8; [**1**] = 1.13 M; [**10**] = 1.15 M; 0.23 mol% **6**.